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None

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B1L
Selected US specifications from IPC sub-class B01D

(54) Measuring the rate of formaldehyde emission from resin-bonded and resin-impregnated materials

(57) An apparatus for measuring the rate of formaldehyde emission from a formaldehyde-containing resin or a material containing such a resin comprises:

a double-walled closed container 11, the inner wall defining a chamber 9, the inner and outer walls defining between them a closed space, and the chamber having an air inlet and an outlet;

a first formaldehyde-absorbing filter 1 (containing e.g. a bed of activated carbon granules) connected to the air inlet;

a second formaldehyde-absorbing filter 21, 23 (containing e.g. a 5% aqueous ammonium acetate solution) connected to the air outlet; and

means (e.g. vacuum pump 31) for inducing a flow of air through said apparatus.

In use a sample of the material is placed in the chamber 9 and the chamber is maintained at a desired temperature and relative humidity; the amount of formaldehyde absorbed by the filters 21, 23 over a measured time period and the rate of formaldehyde emission can thus be determined.

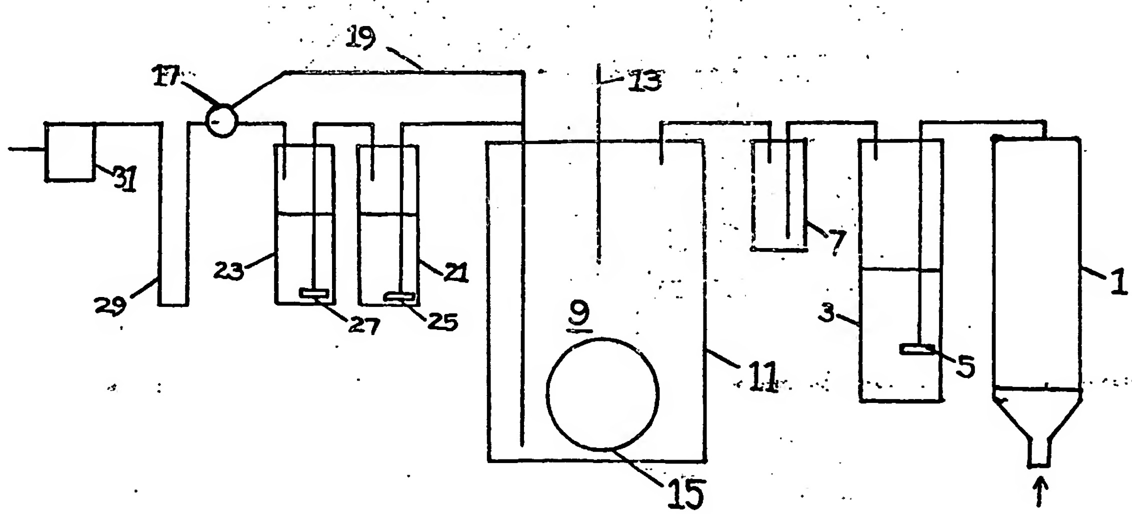

Figure 1

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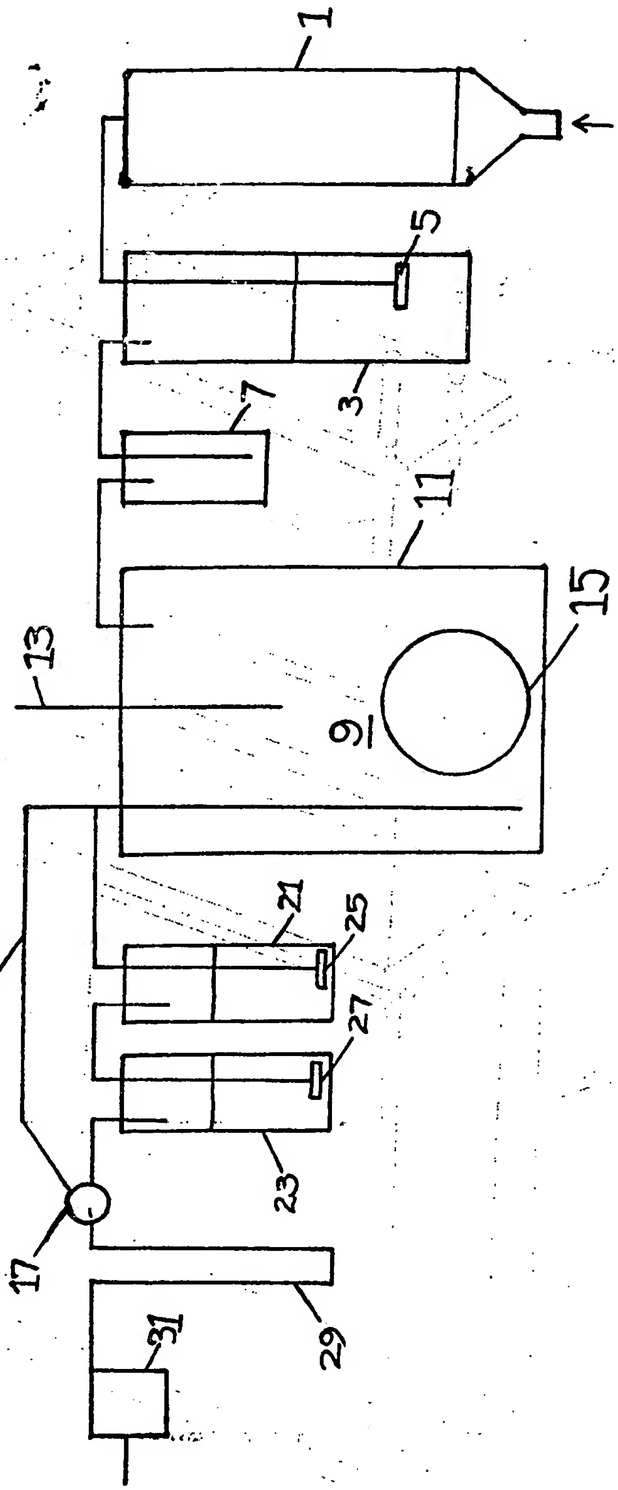

Figure 1

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Figure 2

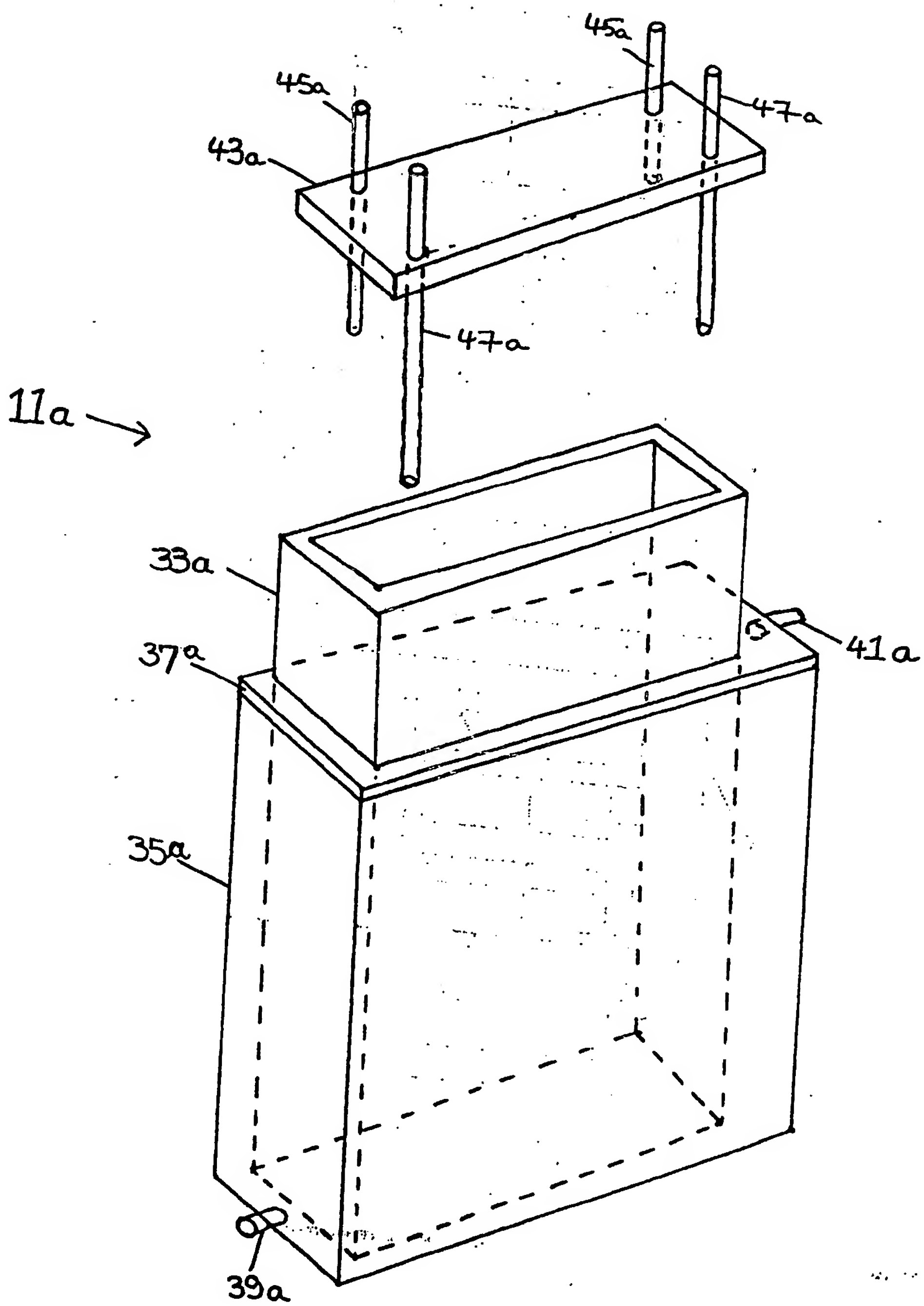
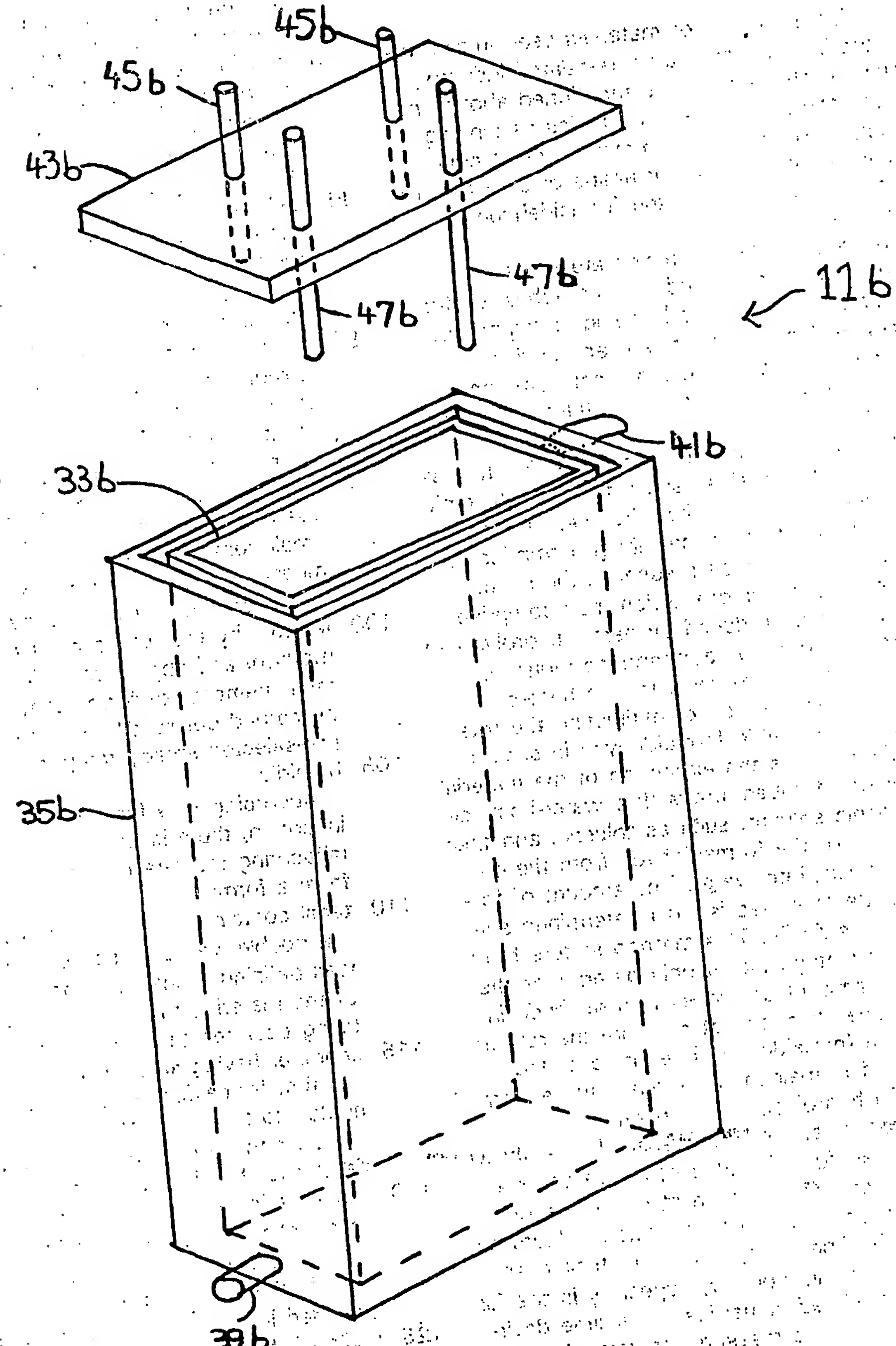


Figure 3



SPECIFICATION

Apparatus and method for measuring the rate of formaldehyde emission from resin-bonded and resin-impregnated materials

The present invention relates to an apparatus and method for measuring the rate of formaldehyde emission from resins or resin-bonded and resin-impregnated materials, such as adhesives, decorative paper foils, lacquers, paints, plyboard, chipboard and medium density fibreboard wherein the resin contains formaldehyde.

A large number of materials used in the furniture industry and furniture-related industry, such as those materials mentioned above, include formaldehyde-based resins as binding agents. Generally the formaldehyde is condensed with phenol, melamine or urea to form the resin, and usually the formaldehyde is used in excess.

Urea-formaldehyde resins are of particular use in the furniture industry as adhesives for wood and for particle bonding in chipboard, medium density fibre board and similar boards. They are also the most common film-forming resins used in acid-catalysed paints and lacquers.

It is known that materials containing formaldehyde-based resins have a tendency to emit formaldehyde during their lifetime. The majority of the emitted formaldehyde comprises the excess formaldehyde present in the resin. However, a minor proportion may comprise formaldehyde produced by partial hydrolysis of the resin caused by atmospheric moisture, especially when the resin is also heated.

One known method of estimating the total amount of available formaldehyde in such a material involves the extraction of the material at elevated temperature with a water-immiscible organic solvent, such as toluene, and then extraction of the formaldehyde from the organic solvent into water. The amount of formaldehyde extracted is then determined spectrophotometrically. This method suffers from the disadvantage that it only determines the absolute amount of excess formaldehyde in the material. It does not measure the rate at which the formaldehyde is emitted or the amount of formaldehyde which may be formed by partial hydrolysis of the resin.

In recent years, medical research has shown that emitted formaldehyde can have adverse physiological effects, even at concentrations below which its well known irritant effects are observable. Therefore, in view of their ever increasing use in industry, especially in the furniture and related industries, it becam desirable to be able to measure the rate of emissi n of formaldehyde from materials bonded [illegible] since the rate of emission vari s with a large number of factors, such as temperature, humidity, porosity and density of the material, and age of the material.

One proposal for measuring the rate of formaldehyde emission from such materials comprises placing a sample of the material in a standard glass desiccator containing a measure volume of distilled water. After a period of time, the amount of formaldehyde contained in the water is determined spectrophotometrically. It is assumed that all the formaldehyde emitted by the material will be absorbed by the water, and that therefore it is possible to calculate accurately the rate of formaldehyde emission.

However, it has been proved experimentally that this assumption is incorrect and that a significant proportion of the emitted formaldehyde will not be absorbed by the water, therefore reducing the accuracy of the method. Moreover, the method suffers from the disadvantage either that it is subject to inaccuracies due to changes in the ambient atmosphere surrounding the desiccator or that it requires the ambient atmospheric conditions to be strictly controlled. This latter requirement generally requires control of the atmosphere of the whole laboratory in which the method is being carried out, which is very costly and normally beyond the means of small companies wishing to perform accurate measurements of formaldehyde emissions.

The present invention provides a method (known by the Applicants as the Dombey method) and apparatus which allows accurate measurements of formaldehyde emissions to be carried out readily and inexpensively at a pre-selected steady temperature and relativ humidity.

According to a first aspect of the present invention, there is provided an apparatus for measuring the rate of formaldehyde emission from a formaldehyde-containing resin or a material containing such a resin comprising:

a double-walled closed container, the inner wall defining a chamber for receiving a sample of the material, the inner and outer walls defining between them a closed space, and th chamber having an air inlet and an air outlet;

a first formaldehyde-absorbing filter connected to the air inlet;

a second formaldehyde-absorbing filter connected to the air outlet; and

means for inducing a flow of air through said first filter, said inlet, said chamber, said outlet and said second filter.

Preferably, a fluid inlet and fluid outlet ar provided in the closed space defined by the walls of the container so that an air-conditioning fluid, such as hot or cold air or water, can be passed through the closed space to bring the chamber to a desired temperature. Advan-

sired temperature, it can be insulated from the ambient atmosphere by the evacuated closed space to maintain the chamber at the desired temperature.

Conveniently, a temperature sensor, such as a thermometer, and/or a hygrometer are located in the chamber whereby the atmospheric conditions in the chamber can be monitored.

Preferably, an air humidity controller is located between the first filter and the chamber air inlet. This may be either an air dryer, for ensuring that the air passing into the chamber is dry, or, more preferably, a humidifier for ensuring that the air passing into the chamber has a controlled moisture content. The humidifier may comprise a conventional impinger having a sintered glass gas distribution head immersed in an aqueous salt solution. In the latter case, it is advantageous to provide a splash trap downstream of the humidifier to prevent any liquid passing into the chamber.

Advantageously, a bypass line is provided whereby air passing out of the chamber outlet can be vented to the atmosphere without passing through the second filter. As will become apparent below, the presence of such a bypass line is useful during the initial stages of use of the apparatus.

The apparatus preferably includes an air flow meter for monitoring the amount of air passed through the chamber during a test.

Preferably, the walls of the container are made of a material having high specific heat and low thermal conductivity. Advantageously the material is also transparent to permit visual inspection of the material under test. Clearly the material used for the container walls should not include a formaldehyde-based resin. A preferred material for the container walls is a polymethylmethacrylate, such as Perspex (Perspex is a registered trade mark). Other suitable materials include cellulose nitrate, cellulose esters, cellulose ethers, polyamides, rigid polyesters, hard rubbers, polypropylene, polytetrafluoroethylene, polystyrene, polycarbonate, polyvinyl acetate, polyvinylchloride, polyvinyl formal, acetal or butyral, polyacrylonitrile, polyvinylidine chloride, polyacrylates, copolymers of the above, glass, resin-bonded glass fiber, ceramics and earthenware.

Conveniently, the gap between the container walls will be between 0.5 and 100mm, th walls will each be between 1 and 15mm thick, and the maximum dimension of the container in any direction will be between 100 and 1000mm.

Advantageously, the chamber has two inlets and two outlets to ensure that the chamber is fully sw pt by air passing therethrough.

Preferably, the first formaldehyde filter is a formaldehyde free, thus avoiding any inaccuracies in the results caused by formaldehyde emissions from paint or furniture in the laboratory.

The second filter preferably comprises at least one, and more preferably two or more, conventional impingers, each have a sintered glass gas distribution head immersed in water or a formaldehyde-absorbing solution, such as a 5% aqueous solution of ammonium acetate.

Preferably, the means for inducing the flow of air through the apparatus is a vacuum pump, most preferably located downstream of all the other components. Alternatively it may comprise a fan or impeller located upstream of all the other components.

According to a second aspect of the present invention, there is provided a method for measuring the rate of formaldehyde emission from a formaldehyde-containing resin or a material bonded therewith comprising:

placing a sample of the material in the chamber defined by the inner wall of a double walled closed container having an inlet and an outlet, the outer and inner walls defining between them a closed space;

maintaining the chamber at a desired temperature and relative humidity;

passing a flow of formaldehyde-free air through the inlet into the chamber;

passing the flow of air exiting from the outlet of the chamber through a formaldehyde-absorbing filter; and

determining the amount of formaldehyde absorbed by the filter over a measured time period whereby the rate of formaldehyde emission can be determined.

Preferably, the air flow exiting from the outlet initially by-passes the filter until an equilibrium state is established in the chamber.

Conveniently, the formaldehyde-free air is treated so that it has a desired moisture content prior to its passage into the chamber.

Advantageously, the method of the present invention is carried out using the apparatus according to the first aspect of the invention.

Where, in the apparatus, the second filter is at least one impinger, the amount of formaldehyde absorbed may be measured spectrophotometrically. For example, the solutions in the impingers may be combined and a colourimetric reagent, such as chromotropic acid or acetylacetone, is added to the combined solutions. The volume of th c loured solution is measured and the absorbance of the coloured solution is measured spectrophotometrically. From these measurements it will be possible to determine the amount of formaldehyde absorbed during the test period. This measurement can then be related t th test sample to give a practically useful formaldehyde emis-

of formaldehyde emission, but it may affect the accuracy of measurement if it is very low or very high. It should therefore be set around an optimum value for the apparatus being used. A convenient optimum rate for use with the apparatus described above is between 0.7 and 1.3 1/min, preferably 1.0 1/min.

Preferably before the test sample is placed in the chamber, the chamber is brought to a desired temperature by passing an air-conditioning fluid, such as hot or cold air or water, through the closed space. Advantageously, thereafter the closed space is evacuated to insulate the chamber from changes in the ambient atmosphere.

Where the material under test is a paint or lacquer, the sample may be provided by coating a glass plate with the paint or lacquer. Where the material under test is a board, it may be used alone as the sample. However, as the sample will be considerably smaller than the board in use, and in use the board will emit substantially all the formaldehyde through its major surfaces, it is advantageous to seal the edges of the sample so that emission only takes place through the major surfaces of the sample. This will thus more closely mimic the conditions of actual use of the board.

The apparatus and method of the present invention have the advantage that they can be used accurately to determine the rate of formaldehyde emission without the need to air-condition the whole laboratory in which the test is being carried out.

Moreover, the test can be carried out under conditions which mimic the normal conditions of use, again without the need to change the conditions in the ambient atmosphere. For instances, on a sunny day, the surface of a board may reach a temperature of at least 50°C and may be exposed to a very moist atmosphere. The rate of formaldehyde emission can readily be measured under these conditions in the apparatus of the present invention.

Further, the results given by use of the present invention are more accurate than those given by the previously used methods, since it is ensured that all the emitted formaldehyde is absorbed and measured.

An embodiment of an apparatus according to the present invention is now described by way of example only, with reference to the accompanying drawings in which:

Figure 1 is a schematic diagram of the apparatus;

Figure 2 is an exploded perspective view of a container for use in the apparatus of Figure 1; and

Figure 3 is an exploded perspective view of an alternative container for us in the apparatus of Figure 1

activated carbon granules for absorbing formaldehyde in the ambient atmosphere. The outlet of filter 1 is connected to the inlet of a first impinger 3 having a sintered glass gas distribution head 5 and containing a saturated aqueous solution of sodium hydrogen sulphate. Air exiting from the first impinger 3 will have a relative humidity of about 50% at 22°C.

The outlet of the first impinger 3 is connected to the inlet of a splash trap 7 for collecting any liquid entrained in the air flow after passage through the first impinger 3.

The outlet of the splash trap 7 is connected to the inlet into the inner chamber 9 of a double-walled container 11, which is described in more detail below. The double-walled container 11 is provided with a thermometer 13 and a hygrometer 15 for monitoring the atmospheric conditions in the chamber 9.

The outlet of the chamber 9 is connected to a three way stopcock 17, either directly along line 19 or via second and third impingers 22 and 23, each of which has a sintered glass gas distribution head 25 or 27 respectively and contains a 5% aqueous solution of ammonium acetate.

The third outlet of the stopcock 17 is connected via an air-flow meter 29 to a vacuum pump 31.

One construction for the double-walled container 11 is shown in Figure 2, to which reference is now made.

The container 11a shown in Figure 2 comprises an inner Perspex box 33a open at one end. The inner box 33a is surrounded by an outer Perspex box 35a which is larger is cross-sectional area than the inner box 33a, but is not as tall as the inner box 33a. Therefore, for the majority of its height the inner box 33a is surrounded by, but spaced from, the outer box 35a. The space between the boxes 33a and 35a is closed by a sheet 37a of Perspex.

An inlet 39a and outlet 41a are provided in the container for connection of the space to a supply of air conditioning fluid, such as water, or a vacuum pump.

The inner box 33a has a removable lid 43a which can be sealingly engaged on the open end of the inner box 33a, for instance by means of toggle clamps (not shown). The lid 43a has in it two air inlet tubes 45a and two air utlet tubes 47a.

Another construction for the double walled container 11 is shown in Figure 3, to which reference is now made. This is similar in construction to the container 11a shown in Figure 2 and therefore is not described in detail. The parts which corresp nd to those shown in Figure 2 are given the same reference numerals, but with th suffix "b" instead of "a".

The main difference between the two con-

the inner box 33b, and the lid 43b seals both the inner box 33b and the space between the inner and outer boxes 33b and 35b.

The container lla of Figure 2 has the advantage that the chamber 9 can be brought to the desired temperature prior to insertion of the sample, but has the disadvantage that the insulation of the inner chamber 9 is not as good as it could be. The container 11b shown in Figure 3 has good insulation but requires that the chamber 9 be brought to the required temperature after insertion of the sample.

In use of the apparatus shown in Figure 1 and Figure 2 or Figure 3, a sample is placed in the chamber 9, with an inlet/outlet pair on either side of the sample so that both sides of the sample are swept by the air flow.

The sample may be a sheet of glass having on one or both of its surfaces a coating of a formaldehyde-containing lacquer, paint, resin-impregnated paper or adhesive. Alternatively, the sample may comprise a sheet of chip or similar board bonded by a formaldehyde-containing resin, the edges of the board having been sealed so that emission only proceeds through its major surfaces.

The chamber 9 is then brought to or maintained at a desired temperature by passage of an air-conditioning fluid, such as hot or cold water, through the inlet 39 and outlet 41. Once the desired temperature is reached, the fluid is removed and the space is evacuated to insulate the chamber 9.

The three way stopcock 17 is set so that air exiting from the chamber by-passes the second and third impingers 21 and 23 by flowing along line 19. The pump is activated and air is allowed to flow through the apparatus until the conditions in the chamber 9 have reached an equilibrium. This will generally take between fifteen minutes and half an hour.

The stopcock 17 is then set so that air exiting from the chamber 9 passes through the second and third impingers 21 and 23. This is allowed to continue for a predetermined time, for instance between 1 and 2 hours. During this time air is drawn from the atmosphere, made formaldehyde-free in the filter 1, humidified to a desired level in the first impinger 3 and dewatered in splash trap 7, and formaldehyde emitted by the sample is swept up into th air stream and fully absorbed in the second and third impingers 21 and 23.

After the predetermined time the pump 31 is turned off and the solutions from the second and third impingers 21 and 23 ar combined and treated with a solution of chromotropic acid or acetylacetone which reacts with formaldehyde to f rm a coloured product. The concentration of the coloured product in the solution is determined spectrophotometrically, and the rate of formaldehyde emission from the sample can be calculated.

It has been found using this method, which the Applicants refer to as the Dombey method after its deviser, the rate of formaldehyde emission varies substantially with temperature. For instance, for some resin-bonded boards, the rate of formaldehyde emission doubles with a rise in temperature of about 7°C. It can thus be seen that by using the Dombey method, which allows careful control of the test conditions, it will be possible to obtain much more accurate measurements than has previously been possible without the need for strict environmental control in the entire laboratory. Moreover, because of the use of the double-walled container, it is not necessary to maintain a continual flow of air-conditioning fluid in order to maintain the desired temperature. Thus a substantial cost saving can be achieved.

CLAIMS

1. An apparatus for measuring the rate of formaldehyde emission from a formaldehyde-containing resin or a material containing such a resin comprising:

a double-walled closed container, the inner wall defining a chamber for receiving a sample of the material, the inner and outer walls defining between them a closed space, and the chamber having an air inlet and an outlet;

a first formaldehyde-absorbing filter connected to the air inlet;

a second formaldehyde-absorbing filter connected to the air outlet; and

means for inducing a flow of air through said first filter, said inlet, said chamber, said outlet and said second filter.

2. The apparatus of claim 1, wherein a fluid inlet and fluid outlet are provided in the closed space defined by the walls of the container so that an air-conditioning fluid, such as hot or cold air or water, can be passed through the closed space to bring the chamber to a desired temperature.

3. The apparatus of claim 1, wherein the closed space is evacuated so that, after the chamber has reached a desired temperature, it is insulated from the ambient atmosphere by the evacuated closed space to maintain the chamber at the desired temperature.

4. The apparatus of any one of claims 1 to 3 wherein a temperature sensor, such as a thermometer, and/or a hygrometer are located in the chamber whereby the atmospheric conditions in the chamber can be monitored.

5. The apparatus of any one f claims 1 to 4, wherein an air humidity controller is located between the first filter and the chamber air inlet.

having a sintered glass gas distribution head immersed in an aqueous salt solution.

8. The apparatus of claim 7, and including a splash trap downstream of the humidifer to prevent any liquid passing into the chamber.

9. The apparatus of any one of claims 1 to 8, wherein a bypass line is provided whereby air passing out of the chamber outlet can be vented to the atmosphere without passing through the second filter.

10. The apparatus of any one of claims 1 to 9, which includes an air flow meter for monitoring the amount of air passed through the chamber during a test.

11. The apparatus of any one of claims 1 to 10, which has two inlets and two outlets to ensure that the chamber is fully swept by air passing therethrough.

12. The apparatus of any one of claims 1 to 11, wherein the first formaldehyde filter is a bed of activated carbon granules.

13. The apparatus of any one of claims 1 to 12, wherein the second filter comprises at least one, and more preferably two or more, conventional impingers, each having a sintered glass gas distribution head immersed in water or a formaldehyde-absorbing solution, such as a 5% aqueous solution of ammonium acetate.

14. The apparatus of any one of claims 1 to 13, wherein the means for inducing the flow of air through the apparatus is a vacuum pump, most preferably located downstream of all the other components.

15. An apparatus for measuring the rate of formaldehyde emission from a formaldehyde-containing resin or a material containing such a resin, substantially as hereinbefore described with reference to the accompanying drawings.

16. A method for measuring the rate of formaldehyde emission from a formaldehyde-containing resin or a material bonded therewith comprising:

placing a sample of the material in the chamber defined by the inner wall of a double walled closed container having an inlet and an outlet, the outer and inner walls defining between them a closed space;

maintaining the chamber at a desired temperature and relative humidity;

passing a flow of formaldehyde-free air through the inlet into the chamber;

passing the flow of air exiting from the outlet of the chamber through a formaldehyde-absorbing filter; and

determining the amount of formaldehyde absorbed by the filter over a measured time period whereby the rat of formaldehyde emission can be d termined.

17. The method of claim 16, wh rein the air flow exiting from the outlet initially bypasses the filter until an equilibrium state is established in the chamber.

its passage into the chamber.

19. The method of any one of claims 16 to 18 which uses an apparatus according to any one of claims 1 to 15.

20. A method for measuring the rate of formaldehyde emission from a formaldehyde-containing resin or a material bonded therewith, substantially as hereinbefore described with reference to the accompanying drawings.

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European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 93 10 4954

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y	US-A-3 203 248 (STUTLER ET AL.)	1,4	G01N1/00
	* column 5, line 48 - line 67; figures 3-8 *	2,3	G01N30/06
	* column 6, line 67 - column 7, line 2 *		
	* column 4, line 30 - line 47; figure 8 *		
A	* column 1, line 49 - line 55 *	9	

Y	JOURNAL OF PHYSICS E. SCIENTIFIC INSTRUMENTS vol. 16, 1983, BRISTOL GB pages 24 - 25 ZIELINSKI 'microsampling valves'	1,4	
	* page 24, column 2, line 6 - line 7 *		
	* page 24, column 2, line 29 - line 30 *		
A	* page 25, column 1, line 7 - line 12 *	8	

A	FR-A-2 040 695 (ELF) * page 2, line 27 - page 3, line 10; figure 1 *	1	

A	US-A-4 199 988 (BODENSEEWERK PERKIN-ELMER)	6,7	
	* column 4, line 45 - line 60; figures 1-2 *		TECHNICAL FIELDS SEARCHED (Int. Cl.5)
	* column 5, line 36 - line 61; figure 3 *		G01N

A	WO-A-9 113 350 (TEKMAR)	1,3,4,9	
	* page 16, line 11 - line 14; figures *		
	* page 5, line 4 - line 10 *		

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	15 JULY 1993	HOCQUET A.P.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
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& : member of the same patent family, corresponding document